



Hidden cycle of dissolved organic carbon in the deep ocean

Christopher L. Follett^{a,b,1}, Daniel J. Repeta^b, Daniel H. Rothman^a, Li Xu^b, and Chiara Santinelli^c

^aLorenz Center, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139; ^bDepartment of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543; and ^cConsiglio Nazionale delle Ricerche, Istituto di Biofisica, 56124 Pisa, Italy

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Marine dissolved organic carbon (DOC) is a large (660 Pg C) reactive carbon reservoir that mediates the oceanic microbial food web and interacts with climate on both short and long timescales. Carbon isotopic content provides information on the DOC source via $\delta^{13}\text{C}$ and age via $\Delta^{14}\text{C}$. Bulk isotope measurements suggest a microbially sourced DOC reservoir with two distinct components of differing radiocarbon age. However, such measurements cannot determine internal dynamics and fluxes. Here we analyze serial oxidation experiments to quantify the isotopic diversity of DOC at an oligotrophic site in the central Pacific Ocean. Our results show diversity in both stable and radio isotopes at all depths, confirming DOC cycling hidden within bulk analyses. We confirm the presence of isotopically enriched, modern DOC cocycling with an isotopically depleted older fraction in the upper ocean. However, our results show that up to 30% of the deep DOC reservoir is modern and supported by a 1 Pg/y carbon flux, which is 10 times higher than inferred from bulk isotope measurements. Isotopically depleted material turns over at an apparent time scale of 30,000 y, which is far slower than indicated by bulk isotope measurements. These results are consistent with global DOC measurements and explain both the fluctuations in deep DOC concentration and the anomalous radiocarbon values of DOC in the Southern Ocean. Collectively these results provide an unprecedented view of the ways in which DOC moves through the marine carbon cycle.

carbon cycle | carbon isotopes | dissolved organic carbon | radiocarbon | oceanography

Radiocarbon is a natural tracer of carbon flow through dissolved organic carbon (DOC) (1). As plankton grow and are consumed by grazers, organic matter with a modern radiocarbon value ($\Delta^{14}\text{C} > -50\text{‰}$) is released into surface waters where it accumulates as semilabile DOC (2–4). Semilabile DOC undergoes net remineralization below the euphotic zone and gradually diminishes in concentration with depth to approximately 1,000 m, below which it appears to vanish. Oceanic profiles of total DOC and DOC radiocarbon ($\text{DOC}\Delta^{14}\text{C}$) are therefore characterized by high values (60–80 μM carbon; -200‰ to -400‰) in surface waters and lower values at depth (35–40 μM ; -400‰ to -550‰) (2). The -200‰ to -300‰ depletion in $\text{DOC}\Delta^{14}\text{C}$ values in surface seawater relative to semilabile $\text{DOC}\Delta^{14}\text{C}$ indicates the presence of a second refractory DOC fraction with an old radiocarbon age. The inverse proportionality between DOC concentration and radiocarbon value in depth profiles suggests that refractory DOC is well mixed throughout the entire water column (2, 3, 5, 6). The origin of the refractory DOC fraction is obscure, but stable isotopes ($\delta^{13}\text{C}$) show little change with depth $\delta^{13}\text{C} = -21.7\text{‰}$ (-23.2‰ to -20.2‰) (2, 7–9), indicating a common, autochthonous planktonic source for both fractions (2).

DOC and $\text{DOC}\Delta^{14}\text{C}$ profiles can be reproduced in a simple two-component model (TCM) that includes a variable amount of semilabile DOC cycling in the upper ocean (<1,000 m) superimposed on a ubiquitous background of radiocarbon-depleted refractory DOC (2, 3). In the TCM, semilabile DOC cycles on

timescales of months to years, whereas refractory DOC cycles over several millennia (2, 3, 10). The TCM provides an excellent 1D representation of DOC and isotope values in seawater.

The simple mixing of two isotopically distinct components implicit in the TCM can be contrasted with the wide range of mass fluxes and isotope values measured in potential sources of marine DOC. These sources include terrestrial organic matter from C_3 and C_4 plants delivered by rivers (1, 4, 11), chemosynthetic organic matter from hydrothermal vent systems (12), organic matter derived from the oxidation of sedimentary methane (13), atmospheric deposition of black carbon from fossil fuel and biomass burning (14, 15), chemoautotrophy in the mesopelagic zone (16), and organic matter released from sinking particles (17–19). Together these sources represent a $\delta^{13}\text{C}$ range of -14‰ to -43‰ , a $\Delta^{14}\text{C}$ range of 150‰ to $-1,000\text{‰}$, and a carbon flux of >3.5 Pg/y. It is unlikely that all of these sources are highly labile and nonaccumulating, and past studies have recognized that deep DOC is most likely a complex mixture of refractory carbon with a range of potential sources and cycling timescales (1, 4, 6, 8, 9, 11, 20). Evidence for the presence of a significant semilabile component within deep sea DOC is lacking (8). Simple isotope mass balance models have been used to explore relationships between the mass and isotopic value of components within deep sea DOC (6, 8), and efforts have been made to isolate DOC components for isotopic characterization (21, 22). Compound and class specific isotope analyses have shown diversity within a very small fraction (1–2%) of DOC, but these studies have not been able to connect specific isotope values to a corresponding inventory or mass flux. Studies based on bulk radiocarbon leave room for dynamic cycling, but with

Significance

Oceanic dissolved organic carbon (DOC) contains as much carbon as Earth's atmosphere, yet its cycling timescales and composition remain poorly constrained. We use serial oxidation experiments to measure the quantitative distribution of carbon isotopes inside the DOC reservoir, allowing us to estimate both its cycling timescales and source distribution. We find that a large portion of deep water DOC has a modern radiocarbon age and a fast turnover time supported by particle dissolution. In addition, stable carbon isotopes allow for diverse sources of carbon, besides microbial production, to quantitatively feed this reservoir. Our work suggests a DOC cycle that is far more intricate, and potentially variable on shorter timescales, than previously envisioned.

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¹To whom correspondence should be addressed. Email: follett@mit.edu.

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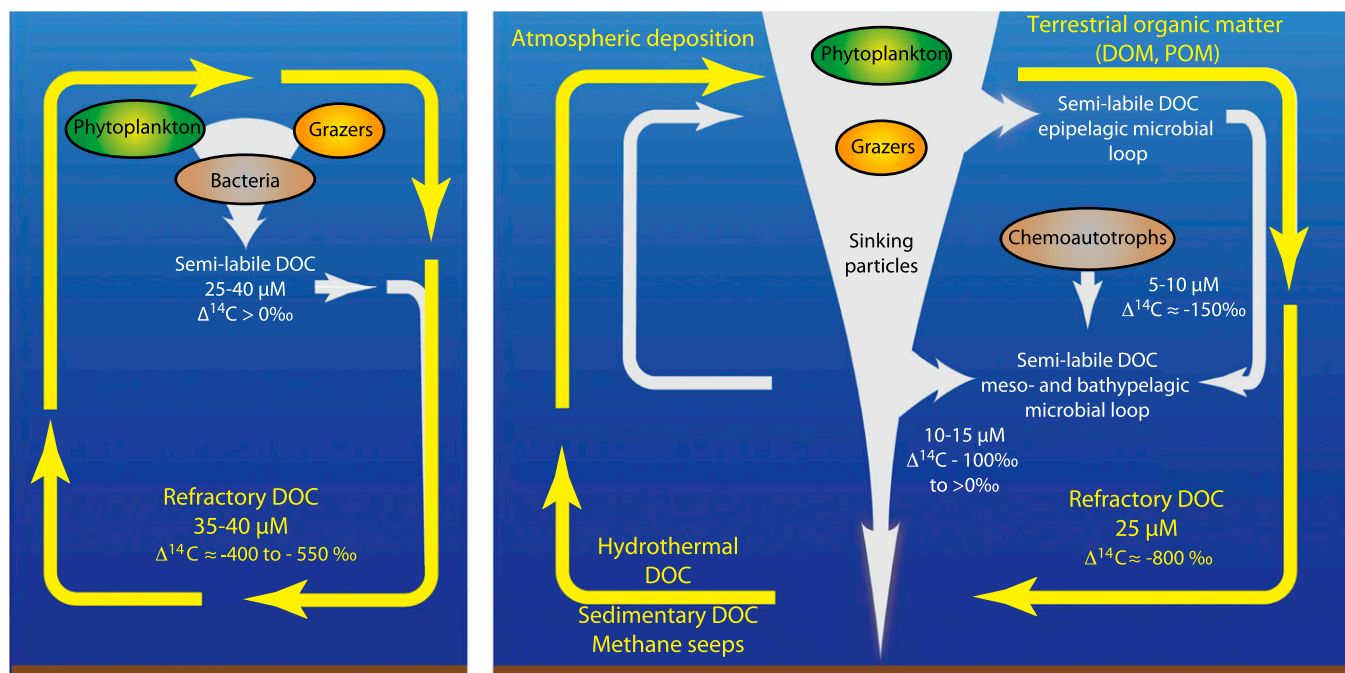


Fig. 3. Physical interpretation. Schematic contrasting DOC cycling in the two-component model (*Left*) and the multicomponent model proposed here (*Right*). In the two-component model, DOC with a modern radiocarbon value is added to surface seawater as a byproduct of microbial carbon production and cycling, such that surface DOC concentrations are relatively high (typically 60–80 μM) and enriched in radiocarbon (–200‰ to –400‰). The semilabile component of DOC (25–40 μM ; $\Delta^{14}\text{C}$ > –50‰) is removed in the mesopelagic ocean, leaving a background fraction of refractory DOC (35–40 μM ; –400‰ to –550‰) that cycles through the ocean over several millennia. Our results (*Right*) show that a large fraction (20–50%) of the sinking particle flux through 500 m, with a modern radiocarbon value from –100‰ to >0‰, accumulates in the deep ocean where it cycles over decadal timescales through the meso- and bathypelagic microbial loops. Chemo- and lithoautotrophy, as well as advection, also contribute to deep semilabile DOC. The refractory fraction of DOC (yellow arrow) has a lower concentration and older mean radiocarbon age than predicted by the TCM. The direct input of refractory carbon, or microbial cycling of semilabile carbon from terrestrial organic matter (atmospheric deposition, rivers, groundwater, desorption from particulate POC), hydrothermal vents, methane, and fossil carbon from seeps, sediments, and the atmosphere is consistent with stable carbon isotopic distributions.

radiocarbon modern material to the deep ocean (17). Global shallow export production estimated from sediment trap measurements and ocean models is approximately 11 Pg C/y, with between 2.3 and 5.5 Pg C/y falling through 500 m (30, 31). The modern radiocarbon value of $\sim 10 \mu\text{M}$ of deep DOC suggests that this material has a turnover timescale less than 50 y and is thus semilabile. If deep, semilabile DOC is in a steady state governed by first-order kinetics, at least 1 Pg C/y flows through this fraction. Our measurements therefore suggest that 20–50% of sinking particulate organic matter is solubilized during export and sequestered for decadal time scales as semilabile DOC within the deep ocean. The carbon flux through deep semilabile DOC is one to two orders of magnitude higher than the flux through DOC calculated from bulk radiocarbon values and dominates the carbon flux through deep sea DOC.

The depleted DOC fraction would include contributions from in situ chemoautotrophy, chemolithotrophy (16, 20, 32), and the advection of DOC from higher latitudes (33–35). It is also likely that some modern and highly depleted carbon is not fully resolved in our measurements and therefore contributes to the depleted fraction. Highly depleted DOC is near 25 μM and -800‰ at 2,000 m. This fraction is significantly depleted relative to the mean $\delta^{14}\text{C}$ value for DOC in the deep ocean (-800‰ vs. -522‰ , respectively) (2), suggesting a radiocarbon age near 12,000 y. Current models suggest that this refractory portion of DOC survives multiple ocean mixing cycles and is in an approximate steady state with modern inputs.

In this case, it is important to realize that the radiocarbon age does not equate to the mean age of the DOC. When a reservoir containing a single component with turnover time τ is in steady state, its mean age equals its turnover time, and the age distribution

is exponential (36). Similar reasoning leads to the following relationship between the radiocarbon age a_r of the reservoir and its turnover time τ (*SI Text*)

$$\tau = \frac{e^{\lambda a_r} - 1}{\lambda}, \quad [3]$$

where λ is the decay constant of radiocarbon. Inserting $a_r = 12,000$ y, we calculate the turnover time τ to be 30,000 y for refractory DOC. This time scale suggests either DOC cycling takes much longer than the currently believed 6,000 y (3) or that an external source of isotopically depleted (pre-aged and potentially labile) carbon supports the refractory DOC.

Global Context

The current form of the TCM is sufficient to explain many open ocean DOC measurements. Chief among its accomplishments are an explanation for the depleted radiocarbon values found in surface ocean DOC and the slow decrease in DOC concentration between the deep North Atlantic and Pacific Oceans. The fundamental tenet of the TCM, that radiocarbon-depleted DOC persists throughout the water column, is well supported by our data. However, certain measurements remain hard to explain unless one allows for a semilabile reservoir of DOC in the deep ocean.

DOC concentrations in the deep ocean for a nominal global ocean transit (Fig. 4) show a general decrease consistent with the slow decay models used to explain them (33). These models use a superposition of material with different first-order decay rates to explain the slowdown of net DOC degradation in the ocean. Decay in these model systems is completely monotonic and fails

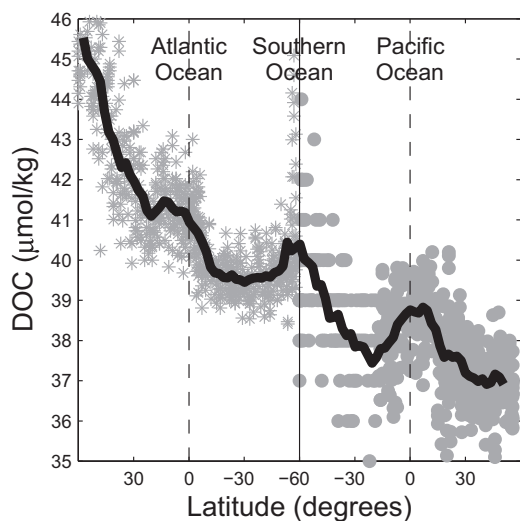


Fig. 4. Changes in DOC concentration (micromoles per kilogram). DOC (34) in the core of the North Atlantic Deep Water along Atlantic transect A16 (*) and in the Circumpolar Deep Water along Pacific transect P16 (•). Water samples were used from the neutral density surfaces consistent with these water masses: $41.25 < \sigma_{3000} < 41.5$ in the Atlantic and $45.85 < \sigma_{4000}$ in the Pacific (34). The running mean across 15° N-S (solid line) is superimposed on the individual DOC measurements (single points). The 1- to 2- μ M increase in DOC at the equator relative to the background trend in both basins is consistent with increased particle export from enhanced primary production at the equator. Data from cdiac.esd.ornl.gov/oceans/RepeatSections/.

to accommodate increases in either bulk DOC concentration or decay rate. Deep ocean transfer of particulate organic carbon (POC) into the DOC reservoir predicts that in areas of higher export production there should be local elevations in deep sea DOC concentrations due to a larger reservoir of semilabile DOC. Global DOC data plotted along density surfaces (34) as it travels from the North Atlantic to the North Pacific Ocean (Fig. 4) provide evidence for these systematic fluctuations. In equatorial regions and the Southern Ocean, we find increases in DOC concentration of 1–2 μ M or 10–20% of the semilabile reservoir. Post-nuclear bomb testing radiocarbon values for the deep semilabile reservoir of DOC suggest a turnover time of <50 y for this portion. Any large impulse of semilabile DOC should thus persist over 15° – 20° N-S based on a mean drift in the deep ocean of 0.3° – 0.4° per year, which is consistent with the observed spatial fluctuations in deep DOC concentrations (Fig. 4). A recent reanalysis of deep Pacific data provides additional evidence that loss of refractory DOC is not a gradual, monotonic process but is localized to mid-depth regions in the North and South Pacific basins (37). Spatial differences in deep transport or release of semilabile DOC could result in the lowered observed DOC concentrations in these regions.

A continual supply of semilabile DOC into the deep ocean from the sinking of large particles should also drive regional fluctuations in deep $\text{DOC}\Delta^{14}\text{C}$ values. The turnover time of semilabile DOC in surface waters is short relative to radioactive decay so that semilabile $\text{DOC}\Delta^{14}\text{C} \approx \text{DIC}\Delta^{14}\text{C}$. $\text{DIC}\Delta^{14}\text{C}$ values can therefore be used as a proxy for semilabile $\text{DOC}\Delta^{14}\text{C}$ (2, 8). Large latitudinal changes in surface water $\text{DIC}\Delta^{14}\text{C}$ (and hence semilabile $\text{DOC}\Delta^{14}\text{C}$) (1) should affect deep sea $\text{DOC}\Delta^{14}\text{C}$ values as semilabile organic matter is cycled through the deep DOC reservoir. This effect should be especially clear as one travels from the Sargasso Sea, through the Southern Ocean, and into the North Central Pacific. Along this journey, surface DIC ranges from $\Delta^{14}\text{C} \sim 50\text{‰}$ to 150‰ in the North Atlantic to $\Delta^{14}\text{C} \sim -100\text{‰}$ to 0‰ in the Southern Ocean and

$\Delta^{14}\text{C} \sim 0\text{‰}$ to 150‰ in the North Pacific (38). Assuming an average background concentration of refractory DOC at $\sim 25 \mu\text{M}$ and $\sim -800\text{‰}$ (Fig. 2), deep semilabile DOC would have a radiocarbon value of $\sim 120\text{‰}$ in the Sargasso Sea, $\sim -80\text{‰}$ in the Southern Ocean, and $\sim 140\text{‰}$ in the North Central Pacific, consistent with measured surface $\text{DIC}\Delta^{14}\text{C}$ values and trends.

If DOC conservatively ages in the deep ocean, its radiocarbon age and that of DIC should change at the same rate. A plot of mean radiocarbon ages of deep water DOC and DIC (Fig. 5) in the Sargasso Sea (2), Southern Ocean (23), and North Central Pacific Ocean (2) shows that, although radiocarbon values in the North Pacific are consistent with conservative aging, the DOC in the Southern Ocean is 500–1,500 y too old (23). Compared with DIC, DOC ages more rapidly as water moves from the North Atlantic to the Southern Ocean and then more slowly as water moves from the Southern Ocean into the North Pacific (23). These trends are straightforwardly explained if semilabile DOC in the deep Sargasso Sea is replaced by surface derived, isotopically depleted, semilabile DOC in the Southern Ocean (more rapid apparent aging of DOC) and then replaced again by modern DOC in the deep North Pacific (slower apparent aging of DOC).

The current paradigm of DOC cycling assumes that the dynamics of DOC in the deep ocean are advectively controlled; that once photosynthetically derived DOC is exported from the surface, it undergoes purely degradative processes (33, 34). This assumption allows one to calculate the net DOC flux from deep concentration gradients and equate it with the gross carbon flux (33, 34). If the dissolution of POC supports a large, semilabile portion of deep DOC, however, then the gross flux is no longer calculable from deep sea gradients in DOC. Under this scenario, the dynamics of deep ocean DOC is affected by surface processes like primary and export production. In this case, the flux through the reservoir could be substantially higher. Regional changes in the global DOC concentration and radioisotope data support this perspective.

Carbon flux from POC to DOC could provide a unifying framework for DOC cycling in disparate environments. POC-DOC transfer from terrestrial sources are believed to affect the bulk $\text{DOC}\delta^{13}\text{C}$ values in the Mid-Atlantic bight, Western North Pacific, and Arctic Ocean (7, 20, 39). Griffith et al. (20) used isotopic evidence to suggest that 30% of deep DOC in Canada Basin water could be terrestrially derived, which would leave the background, refractory, marine-derived DOC fraction at

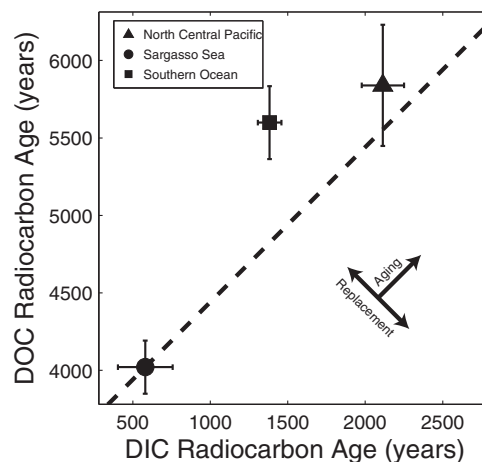


Fig. 5. Bulk radioisotopes and the TCM: DOC radiocarbon age is plotted vs. DIC radiocarbon age for the deep ($>1,000$ m) North Central Pacific Ocean (2), Sargasso Sea (2), and Southern Ocean (23). Mean values are plotted where missing DIC radiocarbon values were linearly interpolated from the depth profile. Error bars represent ± 1 SEM. Points on the dotted line are consistent with conservative aging of both DOC and DIC.

a concentration of 28 μM , well below DOC values in the deep North Pacific but similar to the values determined by our measurements. This amount of background carbon requires that deep Pacific DOC (35–40 μM) contains 7–12 μM semilabile DOC. The Mediterranean Sea may also be unified within the POC-DOC framework. Although the turnover time for Mediterranean deep water is an order of magnitude less than in the global oceans (100s vs. 1,000s of years), deep DOC values reach those found in the North Central Pacific (40). Unique decay conditions may be present. However, low DOC values are consistent with the ultra-oligotrophic surface conditions and low inputs of deep semilabile DOC from particles (41).

Conclusion

The contrast between the large number of diverse sources that supply carbon to marine DOC and the isotopic uniformity measured in stable and radiocarbon analyses and inferred from the TCM has long been considered as a paradox in ocean carbon cycling. Our results show that marine DOC is isotopically diverse, with a broad range of potential sources and cycling timescales. Deep DOC $\delta^{13}\text{C}$ has a range of at least 10‰, allowing for significant contributions from terrestrial organic matter, black carbon, DOC from hydrothermal sources, and

methane seeps. Exceptionally efficient sinks for these external sources of carbon do not need to be invoked to explain the isotopic value of DOC in the deep sea. Furthermore, we suggest that the total flux of carbon through DOC in the deep ocean is at least an order of magnitude higher than the net carbon flux derived from abyssal concentration gradients (33) and bulk radiocarbon measurements (3). Current flux estimates that equate total flux with net flux assume that inputs from the dissolution of sinking particles and chemoautotrophy are small. Our data suggest otherwise. Active cycling of carbon and large annual carbon fluxes through DOC are not restricted to the surface ocean but occur throughout the water column (Fig. 3). Our work suggests a DOC cycle that is far more intricate, and potentially variable on shorter timescales, than previously envisioned.

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